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Technical Report No. 8

I: Experimental Verification of the Mie Theory  
of Light Scattering

Wilfried Heller, Joseph N. Epel and Richard M. Tabibian

Chemistry Department, Wayne University, Detroit

Electron microscopy by

John H. L. Watson

Edsel B. Ford Institute for Medical Research, Detroit

II: "Steric Protection" of Hydrophobic Colloidal  
Particles by Adsorption of Flexible  
Macromolecules

Wilfried Heller and Thomas L. Fugh

Chemistry Department, Wayne University, Detroit

Submitted by

W. Heller, Project Director

Department of Chemistry

Wayne University

August 10, 1954

OFFICE OF NAVAL RESEARCH

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Research on the Size and Shape of Large  
Molecules and Colloidal Particles

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## Introductory Remarks

The present Technical report represents a preprint of two "Letters to the Editor" submitted for publication to the "Journal of Chemical Physics." Part I is a condensation of that part of the experimental work carried out by Mr. Richard Tabibian which was concerned with particle size determinations from the specific turbidity. The extensive data will be reported in a Technical Report which is under preparation (probably Technical Report No. 9) which should be ready for issuance by about the middle of August. Part II is a condensation of that part of the work done by Mr. Thomas L. Pugh which was concerned with the stabilization of colloidal solutions with macromolecular substances. An extensive account of this work is given in Technical Report No. 6 which has been distributed recently.

Wilfried Heller

I. Experimental Verification of the Mie Theory of  
Light Scattering\*

Wilfried Heller, Joseph N. Epel and Richard M. Tabibian  
Chemistry Department, Wayne University, Detroit

Electron microscopy by

John H. L. Watson

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Several thorough investigations published during the past 45 years (1) left little doubt that the Mie theory of light scattering (2) is in essential agreement with the facts. There has, however, been no rigorous quantitative proof which presupposes (a) the use of a system with spherical particles as uniform in size as possible, (b) an exact knowledge of their density and refractive index, (c) an optical precision instrument, and (d) a fairly reliable independent method of comparative size determinations. While one or two of these requirements could be met, not all could be complied with satisfactorily in the past. Polystyrene and polyvinyl toluene latices of remarkably small degree of heterodispersion (3) were used in the present investigation. A separate study by Thomas L. Pugh in this laboratory showed that the colloidal spheres had a density of 1.057 and 1.026 and a refractive index of 1.625 and 1.595 respectively (25°C).<sup>(7)</sup> This note is concerned with particle size determinations from the specific turbidity obtained by transmission measurements using a precision apparatus constructed in this laboratory in conjunction with

K. Herrington (4). Its characteristics pertinent to the data given here are (a) a solid angle of the primary and secondary beam of  $0.7^\circ$  and  $0.8^\circ$  respectively and (b) a quantitative exclusion of primary and secondary parasite light. Since shadow casting showed no perceptible flattening out of the apparently rigid polymer spheres, electron microscopy was used as the independent comparative second method. In view of the wellknown systematic variation of electron-optical diameters with the instrument used (5), an additional set of electron-optical diameters, obtained by Dr. E. P. Bradford of the Dow Chemical Company, was also considered.

The first column in Table I gives the experimental specific turbidities observed at  $5461 \text{ \AA}$ . and extrapolated to zero concentration ( $c$  in  $\text{g. } 100 \text{ g}^{-1}$ ). The second column contains the optical particle diameter,  $D_0$ , calculated by interpolation from the theoretical specific turbidities given in a preceding preliminary note (6). Columns 3 and 4 show the electron microscopic diameters,  $D_p$ , and column 5 defines, by the standard deviation,  $\sigma$ , the spread of the size distribution curve in the latices used. Most of the latter data were compiled in this laboratory.

Excluding from a comparison the unsatisfactory sample with the smallest particle diameter, the average per cent deviation of the electron optical diameters from the optical ones is  $+14.5$  (Watson) and  $+6.8$  (Bradford) for polystyrene, and  $+5.2$  for polyvinyl toluene. The maximum deviation in the latter systems -- which in every respect were more satisfactory

than polystyrene -- amounts to +8.<sup>4</sup>. It is noteworthy that all deviations, except one, are positive, which is possibly accounted for by minute flattening out of the spheres in electron microscopy. (7) The systematic error in electron microscopy should not exceed, but may be as large as  $\pm 5$  per cent and the non-systematic error is assumed to be about  $\pm 1$  per cent. The combined error in measurements of  $\tau$  and  $c$  approximates  $\pm 3$  per cent for particles whose diameters are less than 200  $m\mu$  and  $\pm 2$  per cent for larger particles. Taking all this into account, the agreement between optical and electron optical diameters must be considered as excellent. Consequently, it can be stated, without reservations, that the Mie theory is in quantitative agreement with the facts.

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\*The exploratory first part of this work (J. N. Epel) was supported by a grant from the Research Corporation, the later large scale investigations (Richard M. Tabitian) were supported by the Office of Naval Research.

- (1) Beginning with W. Steubing; Ann. Physik 26, 329 (1908)
- (2) G. Mie; Ann. Physik 25, 377 (1908).
- (3) These lattices were prepared by the Dow Research Laboratories, Midland, Michigan and kindly given to us by Drs. R. S. Spencer and F. Towsley and, more recently, by Dr. J. W. Vanderhoff.
- (4) Unpublished work presented at 116th Meeting of the American Chemical Society, September 1949, Atlantic City, New Jersey.
- (5) See e.g. Ch. H. Gerould; J. Applied Physics 21, 183 (1950).
- (6) W. Heller and W. J. Pangonis; J. Chem. Physics 22, 948 (1954).

- (7) The refractive index decreased with increasing particle size, possibly due to a decrease in the contribution of the highly refractive stabilizing agent adsorbed at the surface of the particles. The values given are extrapolations to zero diameter. Use of the present mean values of a continuing investigation on diameters between 0 and 400 m $\mu$ , 1.607 and 1.588 respectively, would reduce the average per cent deviation between optical and electronoptical diameters to less than 5 per cent for both systems.

Table I

$(\tilde{\nu}/c)_0$ cm <sup>-1</sup>	D <sub>0</sub> μ	D <sub>E</sub> in Bradford	μ Watson	σ
5.1*	58	45	65	8
22.9	109	119	--	4
34.0	132	132	--	2
49.4*	132	135	155	16
42.7	141	144	--	4
59.0*	152	150	180	20
62.7	171	177	--	4
104.2*	206	219	258	10
110.9*	215	223	260	17
109.4*	212	230	218	9
113.0*	217	254	258	10
126.0*	232	252	263	35
126.0*	232	259	289	7
158.4*	262	275	299	47
204	350	---	373	11
246	410	439	--	6
269	446	470	--	5
310	511	535	--	9
331	548	595	--	7
397	705	770	--	11

\*Starred data refer to polystyrene,  
others pertain to polyvinyl toluene.

II. "Steric Protection" of Hydrophobic Colloidal  
Particles by Adsorption of Flexible  
Macromolecules.\*

Wilfried Heller and Thomas L. Pugh

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The two classical principles for protecting non-ionic hydrophobic particles in an aqueous medium are (a) adsorption of capillary active, preferably amphipathic, long chain ions which may provide a sufficiently high surface potential and charge density (e.g. soaps); (b) adsorption of rigid non-ionizing strongly hydrophilic macromolecules (1) which -- after mono-layer formation -- impart upon the particles the typical stability of a hydrophilic colloid (e.g. natural or synthetic polysaccharides and derivatives). The responsible factor may be a critical reduction in the difference of cohesive energy densities of colloid and medium due to indirect hydration. Both principles may apply to a single protective agent (e.g. proteins). A third possibility arose as a consequence of work done by W. Tanaka on the adsorption isotherms of flexible macromolecules (2). It leads to the following picture of the mechanism of adsorption: (a) flexible molecules of the moderately high weight used (up to  $M = 6000$ ) neither "stand up" (like soaps) nor lie flat (like proteins) but most likely assume a configuration roughly described by a V or W (3), i.e. they are anchored into the surface with only a few segments; (b) with increasing surface coverage, and with increasing molecular weight, at equal surface coverage, additional molecules require

more and more time to reach physical contact with the surface (and also to diffuse away from it). Assuming a V configuration, the most probable distance of a terminal segment from the surface proper would be of the order of magnitude of  $10^1$  A.U. Assuming negligible interpenetration of the polymeric peripheries of two colliding colloidal particles -- which appears justified in the light of related results by Flory (4) -- their nearest possible approach would be characterized by a distance of the same order of magnitude. Distances of this order are large enough to make the negative interaction energy of two colloidal particles as small or smaller than their thermal energy. An inability to effectively aggregate, i.e. a stabilization which may be called "steric protection" should therefore be expected in such cases. (5)

Tests were carried out by studying the effect of polyethylene glycols (6) upon the stability of gold sols using a modification of Zsigmondy's gold number. (The same materials had been used for the adsorption experiments.) Protection, towards coagulation by KCl, increased with increasing polymer concentration-without intermediate sensitization -- until an approximately constant optimum was reached at about 1.50 g. of polymer per liter mixture. Table I gives the protective action near this optimum (1.00 g per liter mixture) as a function of M at  $21^{\circ}$ - $24^{\circ}$ C.  $\chi$  represents the concentration of KCl, in millimoles per liter mixture, which leads, after exactly 24 hours, to a red-blue shift in color (transmission) for a Au-concentration of 89 mg per liter mixture.

Table I

M polymer :	600	4000	6000	9000
$\gamma$ * :	$18.0 \pm 2.5$	$22 \pm 5$	$47 \pm 5$	$480 \pm 30$

\*  $\gamma$  in absence of polymer:  $12.5 \pm 2.5$

The protective action increases throughout with M, but an enormous increase begins in the neighborhood of M = 6000. The amount of polymer adsorbed is, according to Tanaka, practically independent of M at M = 6000. Only one plausible explanation of the sudden rise in protective efficiency appears therefore possible, i.e. the attainment at or near this M, of the critical minimum distance between colloidal particles above which "steric protection" becomes fully effective. Since it is very difficult to desorb such high molecular weight material completely, the significance of this type of protection for permanent stabilization of hydrophobic colloids is apparent.

\* This work was carried out with the support of the Office of Naval Research.

- 1) Their hydrophilic monomers are also effective, although considerably less, as the retardation of thixotropic sol-gel transformation by sucrose and aminoacids indicates (W.Heller; Compt. rend. 203, 1507 (1936)).
- 2) for a preliminary publication of some of those results, see W. Heller, and W. Tanaka, Phys. Rev. 82, 301 (1951).
- 3) Recent theoretical work (R. Simha, H. L. Frisch and F. R. Eirich, J. Physical Chem. 57, 581 (1953) seems to support this picture and seems to indicate that the V-configuration is more probable in our case.
- 4) P. J. Flory; J. Chem. Physics 13, 453 (1945).

- 5) M. van der Waarden offered previously essentially the same explanation for the stabilization of charcoal suspensions in organic liquids by means of low molecular weight (up to C<sub>16</sub>) hydrocarbon derivatives. (J. Coll. Sci. 5, 317 (1950)). See also E. L. Mackor and J. H. van der Waals; J. Coll. Sci. 7, 535 (1952).
- 6) Samples, which we purified by reprecipitation were kindly provided by the Carbide and Carbon Chemical Company and also by the Texas Division of the Dow Chemical Company.